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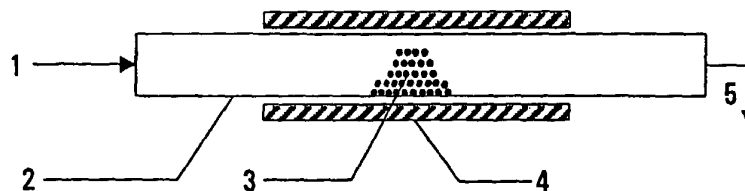
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(54) Title: **LARGE-SCALE SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES BY GROUP VIIIB CATALYSTS PROMOTED BY GROUP VIB METALS**



(57) Abstract: Synthesis of single-walled carbon nanotubes, which comprises contacting a carbon containing material with a catalyst comprising at least two transition metals and a support, wherein at least one transition metal is a group VIIIB element and at least one transition metal is a group VIB element.

**LARGE-SCALE SYNTHESIS OF SINGLE-WALLED CARBON NANOTUBES BY
GROUP VIIIB CATALYSTS PROMOTED BY GROUP VIB METALS**

5 This application is related to U.S. Provisional Patent
Application Serial No. 60/330,805, filed October 31, 2001,
entitled "Large-scale synthesis of single-walled carbon
nanotubes over MoO_x-promoted Co/MgO and Fe/MgO catalysts",
the contents of which are hereby incorporated by reference.

10 Field of the invention

The present invention relates to the synthesis of single-
walled carbon nanotubes (SWNTs), and to catalysts used in
their synthesis.

Background of the Invention

15 Since carbon nanotubes were discovered by Iijima [*Nature*,
354 (1991) 56], many studies on their synthesis and
applications have been engaged in world-wide, due to their
interesting characteristics, such as their unique electrical
and mechanical properties [Yakobson et al., *Am. Sci.* 85
20 (1997) 324]. In other studies, a single-walled carbon
nanotube (SWNT) was shown to be either metallic or
semiconducting depending on its helicity and diameter
[Hamada et al., *Phys. Rev. Lett.* 68 (1992) 1579; Wildoer et
al., *Nature* 391 (1998) 59], a property which may lead to
25 promising applications in molecular electronic devices.
Having the highest Young's modulus and tensile strength
among all known materials also makes carbon nanotubes ideal
components for high strength composite materials [Treacy et
al., *Nature* 381 (1996) 678; Wong et al., *Science* 277 (1997)
30 1971]. In addition, it has been reported that SWNTs display

unusual hydrogen storage ability [Ye et al., *Appl. Phys. Lett.* 74 (1999) 2307; Liu et al., *Science* 286 (1999) 1127].

Three techniques have been employed for the synthesis of SWNTs: A) arc discharge between two graphite electrodes
5 [Iijima et al., *Nature* 363 (1993) 603], B) laser ablation of a graphite target [Guo et al., *Chem. Phys. Lett.* 243 (1995) 49] and C) catalytic decomposition of carbon-containing materials, such as carbon monoxide or hydrocarbons, over metal catalysts [Kong et al., *Chem. Phys. Lett.* 292 (1998)
10 4]. Although the first two methods can produce high quality SWNTs, the quantities produced from both arc discharge and laser ablation are limited, and the associated production costs are high. Future industrial applications of SWNTs, such as hydrogen storage, will necessitate SWNTs in tens of
15 grams, and even kilogram scale. Therefore, the catalytic method may be the best choice for the large-scale production of SWNTs as this method is known to successfully yield multi-walled carbon nanotubes (MWNTs) in large-scale quantities [Tennent et al., *U.S. Patent No. 5,578,584*].
20 However, it is more difficult to produce high quality SWNTs with high yields using the catalytic route. Dai et al. [Chem. Phys. Lett. 260 (1996) 471] were first to report the synthesis of isolated single wall nanotubes from CO decomposition on Mo/Al₂O₃ nanoparticles and Peigney et al.
25 [J. Mater. Res. 12 (1997) 613] subsequently produced a mixture of SWNTs and MWNTs by the decomposition of H₂/CH₄ on Fe/Al₂O₃ nano-composites. SWNTs were also prepared by catalytic decomposition of benzene [Cheng et al., *Appl. Phys. Lett.* 72 (1998) 3282] or ethylene [Hafnet et al.,
30 *Chem. Phys. Lett.* 296 (1998) 195; Flahaut et al., *Chem Phys. Lett.* 300 (1999) 236].

More recently, the synthesis of bulk amounts of high quality SWNTs has been pursued by the decomposition of CH₄ over

Fe/Mo/SiO₂-Al₂O₃ hybrid catalysts [Cassell et al., *J. Phys. Chem. B* 103 (1999) 6484], aerogel Al₂O₃-supported Fe/Mo catalysts [Su et al., *Chem. Phys. Lett.* 322 (2000) 321] and M_xMg_{1-x}O (M=Co, Fe) catalysts [Colomer et al., *Chem. Phys. Lett.* 317 (2000) 83; Bacsa et al., *Chem. Phys. Lett.* 323 (2000) 566], and CO decomposition has been pursued using Co/Mo/SiO₂ catalysts [Kitiyanan et al., *Chem. Phys. Lett.* 317 (2000) 497]. As revealed in these studies, the quality and yield of SWNTs are very sensitive to catalyst supports, metal loading and reaction conditions. Among the various supports, MgO possesses the advantage of being easily removed. Flow rates as high as 6000 cm³/min for CH₄ were used by Cassell et al. although it was not emphasized whether it was a key factor for their synthesis of SWNTs. Bacsa et al. adopted a moderate total flow rate of H₂/CH₄ (250 cm³/min), but the yield of SWNTs was low.

Summary of the Invention

Single-walled carbon nanotubes or a mixture of single-walled and multi-walled carbon nanotubes with high BET surface areas can be produced in accordance with the present invention. The invention also pertains to catalyst preparation and to the controlled growth of SWNTs by variations in catalyst composition.

According to one aspect of the present invention, there is provided a method for the synthesis of single-walled carbon nanotubes, which comprises contacting a carbon containing material with a catalyst comprising at least two transition metals and a support, wherein at least one transition metal is a group VIIIB element and at least one transition metal is a group VIB element.

Preferably, SWNTs are either prepared in a single step process or in a two-step process. In the single step

process, SWNTs are prepared by passing a gaseous mixture of a carbon-containing compound and of a reducing compound, at elevated temperature, over a catalyst comprising a group VIIIIB metal, a group VIB metal and a support. Examples of suitable supports include MgO, SiO₂, SiO₂/Al₂O₃, Al₂O₃, and aerogel Al₂O₃, of which MgO is preferred. The preferred VIIIIB metals are Co, Fe and Ni. Of the VIB metals Cr, Mo and W, Mo is preferred. In the two-step process, the same catalyst is contacted with the reducing agent without a carbon-containing compound being present, and the reduced catalyst is contacted with the carbon-containing compound in a second, separate step.

Brief Description of the Drawings

Figure 1 displays the schematic diagram of a fixed-bed reactor. Identification number 1 represents the entry flow of the carbon containing compound and of the gaseous reducing compound, for example CH₄ and H₂; 2 is the reactor tube; 3 is the catalyst; 4 is the furnace and 5 is the exit flow.

Figure 2 displays the Thermal Gravimetric Analysis (TGA) curves of the raw carbon nanotubes in 10% O₂/Ar, synthesized on catalysts. (a) Co_{0.05}Mg_{0.95}O (comparative); (b) Mo_{0.01}Co_{0.05}Mg_{0.94}O; (c) Mo_{0.025}Co_{0.05}Mg_{0.925}O; (d) Mo_{0.05}Co_{0.05}Mg_{0.9}O

Figure 3 displays the Temperature Programmed Reduction (TPR) spectra of Mo_xCo_yMg_{1-x-y}O catalysts. (a) Co_{0.05}Mo_{0.95}O (comparative); (b) Mo_{0.01}Mg_{0.99}O (comparative); (c) Mo_{0.01}Co_{0.05}Mg_{0.94}O; (d) Mo_{0.025}Co_{0.05}Mg_{0.925}O

Figure 4 displays the Transmission Electron Microscopy (TEM) images of roughly purified nanotubes synthesised on Mo_xCo_yMg_{1-x-y}O catalysts. The images of Figure 4 display the effect that varying the catalyst has on the nanotubes formed. The scale is 100 nm/cm (a) Co_{0.05}Mg_{0.95}O (comparative); (b) and (c)

$\text{Mo}_{0.01}\text{Co}_{0.05}\text{Mg}_{0.94}\text{O}$; (d) and (e) $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$; (f) $\text{Mo}_{0.05}\text{Co}_{0.05}\text{Mg}_{0.9}\text{O}$; (g) $\text{Mo}_{0.075}\text{Co}_{0.05}\text{Mg}_{0.875}\text{O}$; (h) $\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$

Figure 5 displays the low frequency Raman spectra of roughly purified materials synthesized on $\text{Mo}_x\text{Co}_y\text{Mg}_{1-x-y}\text{O}$ catalysts. (a) $\text{Co}_{0.05}\text{Mg}_{0.95}\text{O}$ (comparative); (b) $\text{Mo}_{0.01}\text{Co}_{0.05}\text{Mg}_{0.94}\text{O}$; (c) $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$; (d) $\text{Mo}_{0.05}\text{Co}_{0.05}\text{Mg}_{0.9}\text{O}$; (e) $\text{Mo}_{0.075}\text{Co}_{0.05}\text{Mg}_{0.875}\text{O}$; (f) $\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$

Figure 6 displays the Transmission Electron Microscopy (TEM) images of roughly purified materials synthesized on $\text{Mo}_x\text{Fe}_y\text{Mg}_{1-x-y}\text{O}$ catalysts. The scale is 100 nm/cm. (a) $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$ (comparative); (b) and (c) $\text{Mo}_{0.01}\text{Fe}_{0.05}\text{Mg}_{0.94}\text{O}$; (d) $\text{Mo}_{0.025}\text{Fe}_{0.05}\text{Mg}_{0.925}\text{O}$; (e) $\text{Mo}_{0.05}\text{Fe}_{0.05}\text{Mg}_{0.9}\text{O}$

Figure 7 displays the low frequency Raman spectra of roughly purified materials synthesized on $\text{Mo}_x\text{Fe}_y\text{Mg}_{1-x-y}\text{O}$ catalysts. (a) $\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$ (comparative) and (b) $\text{Mo}_{0.01}\text{Fe}_{0.05}\text{Mg}_{0.94}\text{O}$

Detailed Description of the Invention

Preparation of the single-wall carbon nanotubes

SWNTs are prepared by heating the catalyst, for example in an amount of from about 0.2 to 0.5g, which is preferably in powder form, under a flow of a gaseous mixture comprising one or more carbon containing compounds and, optionally, one or more reducing compounds, such as hydrogen or formaldehyde. The carbon containing compound and the reducing compounds are preferably present in a molar ratio of from 8:1 to 1:4 and total flow rate of the gaseous mixture is preferably about 250 cm^3/min . Flow can be controlled by the use of flowmeters. Carbon nanotubes start growing as soon as the group VIIIB metal is reduced. The concentration of the reducing gaseous compound in the total feed gas is preferably at least 5%, more preferably at least 10% and most preferably at least 20%. There is no upper

limit to the concentration of the reducing gaseous compound as long as carbon-containing compounds still remain in the reactor. Preferably, the furnace temperature is linearly increased up to between 1198K and 1373K, at a rate between 1
5 and 40 K per minute. More preferably, the catalyst is heated to about 1273K at rate of about 5K/min. The reactor is held at the final temperature for 2 min. Subsequently, the flow of the gaseous mixture is stopped, and the resulting nanotube/catalyst product is optionally cooled
10 down in a flow or under an atmosphere of an inert, oxygen-free gas, for example H_2 .

It is also possible to reduce the salts to form the catalyst before the catalyst is used in the production of SWNTs. This can be done by passing a reducing gas such as H_2 or H_2CO
15 over the heated catalyst. Thereafter, nanotubes can be made by passing a carbon-containing gas over the heated catalyst without added hydrogen. This embodiment is less preferred, however, as the ratio of the desired SWNTs to MWNTs decreases.

20 The carbon source used for catalytic decomposition to form SWNTs can be selected from any organic carbon containing compounds, or certain oxides of carbons, that are in the gas phase under the reaction conditions. Preferably used are aliphatic hydrocarbons, aromatic hydrocarbons, oxygen
25 containing hydrocarbons and mixtures thereof. The carbon source can be either saturated or unsaturated. Examples of appropriate carbon sources include methane, ethane, propane, butane, benzene, butene, cyclohexane, ethylene, acetylene, and carbon monoxide, of which methane is preferred.

30 Once the SWNT production is complete, acid can be used to remove the catalyst particles from the SWNTs formed. The acid reacts with the metallic catalyst, rendering it soluble. The raw nanotubes are preferably immersed and

stirred in the acid for 5 to 8 hours. The nanotubes can then be filtered, washed with water and dried in an oven. Inorganic acids are preferred. Suitable examples of acids include HNO₃, HCl, and H₂SO₄. Preferably, a 65% solution is
5 used.

The growth of nanotubes can be carried out in either a fixed-bed or a fluidised-bed reactor. Both reactor types display similar quality and yield of SWNTs. A plurality, say two or three or more, of these reactors can be linked in
10 series. A standard reactor is depicted in Figure 1

The quantity of carbon nanotubes can be determined by Thermal Gravimetric Analysis (TGA). The raw material (without acid purification) is calcined in a flow of 10% O₂/Ar, with a heating rate of 4K/min. The yield of carbon
15 materials is defined as:

$$Y_{\text{carbon nanotubes}} = (W_{\text{initial}} - W_{\text{left}}) / W_{\text{left}} \times 100\%$$

where W_{initial} and W_{left} are the weight left at 473K and 1073K respectively. W_{left} is taken as the weight of the catalyst after carbon materials are burnt out in O₂. As shown in
20 Figure 2, the yield of carbon nanotubes obviously increases with the increase of molybdenum content.

The unrefined SWNTs can also be characterised by TEM, Raman spectrometry and BET surface area analysis.

The presence of the group VIB metal promoter remarkably
25 increased the yield and improved the quality of the SWNTs obtained. The generation rate of SWNTs was raised in some instances at least 10 times and the formation of amorphous carbon was suppressed. There is an optimum content of group VIB and group VIIIB metals, beyond which multi-walled carbon
30 nanotubes are formed. Other transition elements, alone or in mixtures, may also be added to Co/MgO, Fe/MgO or Ni/MgO

catalysts as promoters, in place of or in addition to Mo, to yield SWNTs. Examples include the other two stable group VIB metals, chromium and tungsten.

Preparation of the catalyst

- 5 The catalyst is preferably prepared by a wet mechanical mixing followed by combustion synthesis. One or more group VIB metal salts and one or more group VIIIB metal salts are weighed and mixed together with a salt of a catalyst support in the desired molar ratio as in, for example, $\text{Mo}_x\text{Co}_y\text{Mg}_{1-x-y}\text{O}$ or $\text{Mo}_x\text{Fe}_y\text{Mg}_{1-x-y}\text{O}$, when Mo is used as the Group VIB metal and Co or Fe are used as the Group VIIIB metal. The molar ratio of group VIIIB metal to group VIB metal is preferably in the range of 5:1 To 2:3, and the ratio of group VIIIB metal to catalyst support is preferably in the range of 1:10 to 1:100
- 10 Examples of suitable Group VIIIB metal salts include $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Examples of suitable Group VIB salts include $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, ammonium chromate, ammonium tungstate, ammonium heptamolybdate, and chromium nitrate. $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ is preferred as catalyst support
- 15 salt. A swelling agent, for example citric acid or urea, and several drops of distilled water, whose amount depended on the weight of the mixture, can be added. Preferably, 2 to 3 ml of water is added per 10 grams of catalyst. The mixture is ground until it is uniform and it is then heated
- 20 between 673 and 973K for a period of up to 10 minutes. The combustion synthesis is preferentially carried out at 823K for 5 minutes. The mixture is then cooled to room temperature and the obtained foamy material is ground once more to obtain a fine powder of the desire catalyst.
- 25
- 30 The catalyst can also be prepared without a swelling agent by mechanically mixing a group VIB salt with the salts of the group VIIIB metal and of the support, followed by

addition of water. The remaining steps of the process are then carried out as described above.

Discussion

The combination of Co or Ni with MgO supports in catalysts is advantageous for producing carbon nanotubes. Without wishing to be bound by any theory, this may be due to the easy formation of fine Co or Ni nanoparticles. A solid solution is easily formed between CoO and MgO due to the approximate equality of the radii of Co^{2+} and Mg^{2+} ions, which makes the reduction of CoO difficult, as shown in Figure 3a, as CoO is embedded inside the support. In Mo-containing catalysts, molybdenum may aggregate at the edges of the cobalt particles, as revealed in Co-Mo/ Al_2O_3 catalyst studies by Niemantsverdriet [*Stud. Surf. Sci. Catal.* 79 (1993) 387], which studies were directed to purposes unrelated to the production of SWNTs. This may prevent the complete inlay of Co^{2+} into Mg^{2+} lattice and lead to an increase of Co^{2+} particles available for reduction. The reduction behavior of Mo-Co bimetallic catalysts is complex (Figures 3c and d). However, the low temperature peak below 873K may be ascribed to the reduction of CoO_x and the high temperature peaks to MoO_x . It is obvious that with the addition of MoO_x , the reduction peak of CoO_x became stronger, especially for the $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$ catalyst, indicating that more CoO_x was reduced to metallic Co. As revealed in Table 1 below, the yield of carbon nanotubes over $\text{Co}_{0.05}\text{Mg}_{0.95}\text{O}$ is only 11% while it reaches 114.3% over $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$.

Table 1: The yields and prop rties of carbon nanotubes over $\text{Mo}_x\text{Co}_y\text{Mg}_{1-x-y}\text{O}$ catalysts

Catalysts ($\text{Mo}_x\text{Co}_y\text{Mg}_{1-x-y}\text{O}$)	BET of catalysts (m^2/g)	Yield of nanotubes (%)	BET of roughly purified nanotubes (m^2/g)
$\text{Co}_{0.05}\text{Mg}_{0.95}\text{O}$ (comparative)	145.4	11	856.9
$\text{Mo}_{0.01}\text{Co}_{0.05}\text{Mg}_{0.94}\text{O}$	176.5	41.1	703.7
$\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$	162.9	114.3	685.2
$\text{Mo}_{0.05}\text{Co}_{0.05}\text{Mg}_{0.9}\text{O}$	140.8	215.1	533.2
$\text{Mo}_{0.075}\text{Co}_{0.05}\text{Mg}_{0.875}\text{O}$	107.1	261.4	496
$\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$	N.A.	204.4	621.4
$\text{Mo}_{0.045}\text{Co}_{0.09}\text{Mg}_{0.865}\text{O}$	N.A.	248.9	517.7
$\text{Mo}_{0.07}\text{Co}_{0.07}\text{Mg}_{0.86}\text{O}$	119.6	246.5	450.7
$\text{Mo}_{0.09}\text{Co}_{0.09}\text{Mg}_{0.82}\text{O}$	117.5	263.7	370.7

N.A. - not measured.

The formation of SWNTs was confirmed by TEM image, as shown
 5 in Figure 4. Besides SWNT bundles, many individual tubes
 were also formed. The bundles of these SWNTs are not uniform
 and tight, compared to those synthesized by arc discharge or
 laser ablation. This results in the high BET surface areas,
 such as $685.2 \text{ m}^2/\text{g}$ in the roughly purified sample prepared
 10 from $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$, which is higher than that of SWNT
 samples prepared by laser ablation ($285 \text{ m}^2/\text{g}$) [Ye et al.,
Appl. Phys. Lett. 74 (1999) 2307]. The low frequency Raman
 spectrum found in Figure 5 exhibits unambiguously the

characteristic frequencies of SWNTs, due to the A_{1g} radial breathing mode. It is interesting to note that the strong peak shifts to higher wavenumber when the Mo content is increased. This reveals that the tube diameter of SWNTs decreases with the increase of Mo content, according to the equation [Alvarez et al., *Chem. Phys. Lett.*, 316 (2000) 186]:

$$\nu \text{ (cm}^{-1}\text{)} = 6.5 + 232/d \text{ (nm)}.$$

The tube diameters calculated are in the range of 1.07–1.25 nm.

It should be mentioned that very few carbon nanotubes were formed over $\text{Mo}_x\text{Mg}_{1-x}\text{O}$ catalysts under our synthesis conditions. The modification of Mo on Co will also isolate the metal Co particles and inhibit the aggregation of metal particles, as exists in other bimetallic catalysts [Tang et al., *Catal. Lett.* 59 (1999) 129]. It has been proposed that large metal particles would be inactive for the formation of SWNTs [Su et al., *Chem. Phys. Lett.* 322 (2000) 321]. The addition of appropriate amount of molybdenum to Co/MgO may thus increase the number of metal Co particles suitable for the growth of SWNTs. It is suggested that the SWNTs may be predominantly formed through the "base growth" mechanism, in which metal particles responsible for the nanotube nucleation and growth are attached to the support surfaces. The strong interaction between metal particles and support is thus believed to be beneficial to the growth of SWNTs [Su et al., *Chem. Phys. Lett.* 322 (2000) 321]. Nevertheless, if the content of molybdenum is elevated too much, it may weaken the interaction between metallic Co and MgO support, and a larger metallic Co particles could easily be formed, leading to the growth of MWNTs. With the increase of cobalt content, the similar case occurred, so more and more MWNTs were formed, as observed by TEM in Figures 4 f) and g).

Therefore, a limit to Co and Mo content exists for the growth of SWNTs. $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$ is a good choice for the synthesis of SWNTs, with both good yield and good selectivity. With lower quality requirements,

5 $\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$ can be used.

For Fe-based ($\text{Mo}_x\text{Fe}_y\text{Mg}_{1-x-y}\text{O}$) catalysts, the promotion function of Mo to the yield of SWNTs was also exhibited as shown in Table 2.

Table 2: Yields of carbon nanotubes prepared with $\text{Mo}_x\text{Fe}_y\text{Mg}_{1-x-y}\text{O}$ catalysts

Catalysts ($\text{Mo}_x\text{Fe}_y\text{Mg}_{1-x-y}\text{O}$)	Yield of nanotubes (%)
$\text{Fe}_{0.05}\text{Mg}_{0.95}\text{O}$ (comparative)	24.0
$\text{Mo}_{0.01}\text{Fe}_{0.05}\text{Mg}_{0.94}\text{O}$	64.6
$\text{Mo}_{0.025}\text{Fe}_{0.05}\text{Mg}_{0.925}\text{O}$	128.9
$\text{Mo}_{0.05}\text{Co}_{0.05}\text{Mg}_{0.9}\text{O}$	204.8

Fewer SWNTs were formed over single Fe-based catalysts as revealed by the TEM and Raman spectra shown in Figures 6 and 7. SWNTs were mainly formed with the addition of small
 15 amounts of Mo. However, compared with Mo-Co catalysts, more MWNTs were observed over Mo-Fe catalysts.

Financial advantages

One of the advantages realised by the present synthesis route is that the costs associated with the production of
 20 the SWNTs is very low, estimated to be about S\$2.5-10.0 (Singapore dollars) per gram of the roughly purified SWNTs.

If the effluent gas is recycled and large-scale reactors are used, it is believed that the cost could be further decreased. Compared with the average prices asked by suppliers - (S\$180 per gram of the raw SWNTs and S\$1800 per gram of highly purified SWNTs), this method may be the most economical way to synthesize single-walled carbon nanotubes in large scale, and it should be useful for future industrial applications.

Economical estimation:

Sample	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{H}_{24}\text{Mo}_7\text{N}_6\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Citric Acid
		O		
Price	110S\$/kg	51.8S\$/kg	323.9S\$/kg	59.3S\$/kg

10

Gas	Methane	Hydrogen
Price	82.3S\$/M ³	5.1S\$/M ³

According to the above market price of each reagent and gas, we estimated the value of per gram raw single-walled carbon nanotubes as following:

15 The price of 1g $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$ catalyst is S\$0.433

The price of gas (methane and hydrogen) in above experiment is about S\$1.15

The cost of raw single-walled carbon nanotubes prepared using this catalyst is thus about S\$3.8 per gram. After purification, the cost of roughly purification SWNTs is about 7.1 S\$/gram.

20

If the $\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$ catalyst is used to produce SWNTs with a little lower quality, such as in example 6, the cost of raw single-walled carbon nanotubes decreases to 2.7 S\$/g. After purification, the cost of roughly purified SWNTs
5 lowers to 4S\$/g.

All documents cited or referred to above are to be hereby incorporated by reference.

Examples

The following specific examples are provided to illustrate
10 the invention. It will be understood, however, that the specific details given in each example have been selected for purpose of illustration and are not to be construed as a limitation on the invention.

Example 1

15 10g of $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, 0.6g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.073g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 4g of citric acid were mixed with 2 ml of deionized water. The mixture was stirred, ground until it was uniform and subsequently placed in an oven held at 550°C for about 5 min. The mixture was then cooled to room
20 temperature. A foamy material obtained was ground to a fine powder of $\text{Mo}_{0.01}\text{Co}_{0.05}\text{Mg}_{0.94}\text{O}$.

300mg of the $\text{Mo}_{0.01}\text{Co}_{0.05}\text{Mg}_{0.94}\text{O}$ was placed in the centre of a quartz tube located in a tube furnace. A gas mixture of H_2 and CH_4 with molar ratio of $\text{H}_2:\text{CH}_4$ (4:1) and a total flow
25 rate of 250 cm^3/min was introduced through mass flowmeters. The furnace temperature was linearly increased up to 1000°C at rate of 5°C/min and held at 1000°C for 2 min. Then CH_4 was turned off and the sample was cooled down to room temperature in a flow of H_2 .

Raw carbon nanotubes were obtained and were purified by immersing them in 150ml of 65% HNO_3 solution. The mixture was stirred for about 8 h to dissolve the catalyst. The solution was then filtered and washed with distilled water several times. It was dried for 6 hours in an oven at 120°C . Roughly purified single-walled carbon nanotubes were obtained. Thermal Gravimetric Analysis (TGA) of the SWNT sample is shown in Figure 2.

Example 2

10g of $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, 0.614g of $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, 0.186g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 4g of citric acid were mixed with 2 ml of de-ionized water. The mixture was stirred, ground until it was uniform, and subsequently placed into an oven held at 550°C for about 5 min. The mixture was then cooled to room temperature. The mixture was ground to a fine powder of $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$. Analysis of the catalyst before the production of nanotubes was made through Temperature Programmed Reduction (TPR), as shown in Figure 3. This information is used to qualify the availability of metal particles in the catalyst that can interact with reactants in the gas phase.

In the TPR who's results are shown in Figure 3, various catalyst samples were pretreated under argon at 973K for 30 minutes and then cooled down to 373K and kept at this temperature. The carrier gas was then replaced by 10% H_2 +argon mixture and the temperature was increased to 1273K at a rate of 10K/min. A gas chromatograph was used to measure the amount of consumed H_2 . This analysis displays the reduction of the group VIIIB metal by hydrogen at different temperatures.

Example 3

Following the same procedure of Example 2 and using 10g of $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, 0.887g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.269g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 4g of citric acid and , the $\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$ catalyst was prepared.

5 Example 4

10g of $(\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$, 0.838g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 0.073g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and 4g of citric acid were mixed with about 2 ml of de-ionized water. Through the same procedure as in Example 1, $\text{Mo}_{0.01}\text{Fe}_{0.05}\text{Mg}_{0.94}\text{O}$ catalyst and single-walled carbon
10 nanotubes were obtained.

Example 5

200mg of $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$ as prepared in Example 2 was placed in the centre of a horizontal quartz reactor. A gas mixture of H_2 and CH_4 with a molar ratio of $\text{H}_2:\text{CH}_4$ (4:1) and
15 a total flow rate of $250 \text{ cm}^3/\text{min}$ was introduced through mass flowmeters. The furnace temperature was linearly increased up to 1000°C at a rate of $5^\circ\text{C}/\text{min}$ and held at 1000°C for 2 min. Then CH_4 was turned off and the sample was cooled down in a flow of H_2 . About 0.324g of SWNTs were obtained. Tables
20 1 and 2 display the results obtained when the process above is carried out with various catalysts.

Example 6

Using 200mg of the $\text{Mo}_{0.035}\text{Co}_{0.07}\text{Mg}_{0.895}\text{O}$ catalyst of Example 3 and following the same procedure of Example 5,
25 0.46g of raw single-walled carbon nanotubes were produced.

Example 7

Using 200mg of a $\text{Mo}_{0.025}\text{Fe}_{0.05}\text{Mg}_{0.925}\text{O}$ catalyst and following the same procedure of Example 5, 0.354g of raw single-walled carbon nanotubes were obtained.

Example 8

- 200mg of the $\text{Mo}_{0.025}\text{Co}_{0.05}\text{Mg}_{0.925}\text{O}$ catalyst of Example 2, was put into the reactor for carbon nanotube fabrication. The flow rates of CH_4 and H_2 were $50 \text{ cm}^3/\text{min}$ and $200 \text{ cm}^3/\text{min}$,
5 respectively. The furnace temperature was linearly increased up to 1000°C at rate of $5^\circ\text{C}/\text{min}$ and held at 1000°C for 2 min. Then CH_4 was turned off and the sample was cooled down in a flow of H_2 . 0.324g of raw SWNTs were obtained.

Example 9

- 10 Other catalysts with different Mo, Co or Fe contents were prepared by the change of the amount of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, then following the same procedure in Example 2.

Example 10

- 15 Using different $\text{A}_x\text{B}_y\text{Mg}_{1-x-y}\text{O}$ ($\text{A} = \text{Mo}$, $\text{B} = \text{Co}$ or Fe) catalysts and following the same procedure of Example 5, single-walled carbon nanotubes can be produced with varying yields. Examples of these are illustrated in Tables 1 and 2

Claims

1. A method for the synthesis of single-walled carbon nanotubes, which comprises contacting a carbon containing material with a catalyst comprising at least two
5 transition metals and a support, wherein at least one transition metal is a group VIIIB element and at least one transition metal is a group VIB element.
2. The method according to claim 1, wherein the group VIIIB metal is selected from the group consisting of Co, Fe,
10 and Ni.
3. The method according to claim 1, wherein said group VIB metal is selected from the group consisting of Cr, Mo, and W.
4. The method according to claim 1, wherein the molar ratio
15 of group VIIIB metal to group VIB metal is in the range of 5:1 To 2:3, and the ratio of group VIIIB metal to catalyst support is in the range of 1:10 to 1:100.
5. The method according to claim 1, wherein the catalyst support is selected from the group consisting of MgO,
20 SiO₂, Al₂O₃, a mixture of SiO₂ and Al₂O₃, and aerogel Al₂O₃.
6. The method according to claim 5, wherein the catalyst support is MgO.
7. The method according to claim 1, wherein the catalyst comprises Mo as the group VIB element, Co as the group
25 VIIIB element, and MgO as the support.
8. The method according to claim 1, wherein the catalyst comprises Mo as the group VIB element, Fe as the group VIIIB element, and MgO as the support.

9. The method according to claim 1, where the carbon-containing material is selected from methane, ethane, propane, butane, benzene, butene, cyclohexane, ethylene, acetylene, and carbon monoxide.
- 5 10. The method according to claim 1, wherein the carbon containing material is admixed with one or more reducing gaseous compounds.
11. The method according to claim 10, wherein the catalyst is reduced and the single walled nanotube is grown in a
10 single step.
12. The method according to claim 10, wherein the reducing gaseous compound is hydrogen gas or formaldehyde.
13. The method according to claim 10, wherein the molar ratio of reducing gaseous compound to gaseous carbon containing
15 compound is from 8:1 to 1:4 and the gas flow rate is from 10 to 100 litres per hour per grams of catalyst.
14. The method according to claim 10, wherein the reducing gaseous compound is present in a concentration of at least 5%, in respect to the carbon containing gas.
- 20 15. The method according to claim 1, wherein the catalyst is contacted with a reducing gaseous compound prior to being contacted with the carbon containing material.
16. The method according to claim 15, wherein the reducing gaseous compound is hydrogen gas or formaldehyde.
- 25 17. The method according to claim 1, wherein the catalyst is contacted with the carbon containing material at temperatures of from about 1198K to about 1373K.
18. The method according to claim 17, wherein the temperature is increased over time during the synthesis.

19. The method according to claim 18, wherein the temperature increase is at a rate of from about 1K per minute to about 40K per minute.
20. The method according to claim 18, wherein the temperature increase is at a rate of 5K per minute, and wherein the temperature is increased up to 1273K.
21. The method according to claim 1, wherein the catalytic decomposition is carried out in a fixed-bed reactor.
22. The method according to claim 1, wherein the catalytic decomposition is carried out in a fluidised-bed reactor.
23. The method according to claim 21, wherein several fixed-bed reactors are connected in series.
24. The method according to claim 1, wherein the single wall carbon nanotubes are separated from the catalyst by immersion in an inorganic acid solution.
25. The method according to claim 24, wherein the inorganic acid solution comprises HNO_3 , HCl , H_2SO_4 or mixtures thereof.

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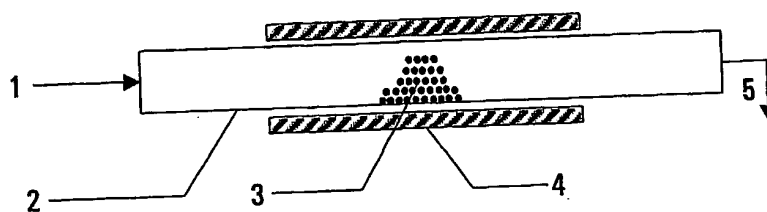
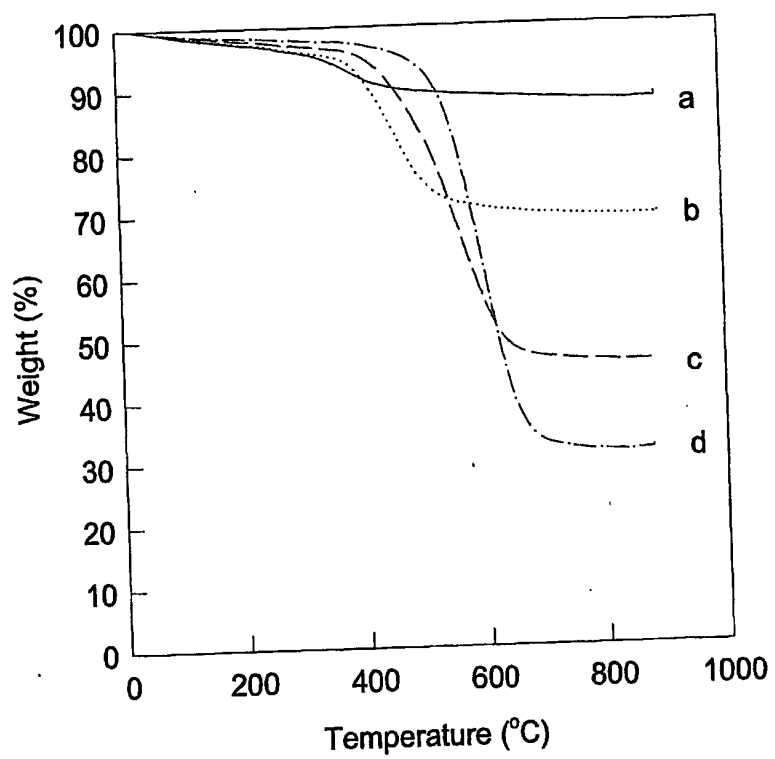
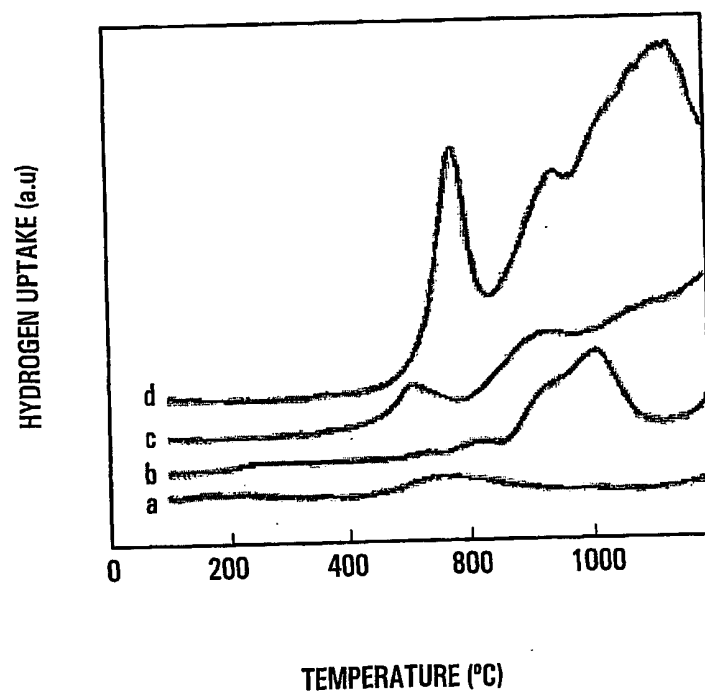


FIG. 1

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**FIG. 2**

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**FIG. 3**

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FIG. 4A



FIG. 4B



FIG. 4C



FIG. 4D



FIG. 4E



FIG. 4F

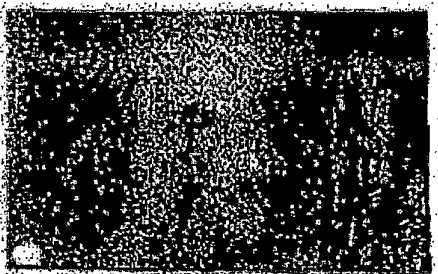


FIG. 4G

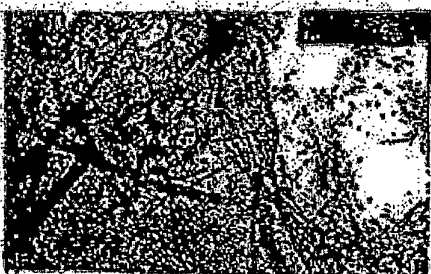
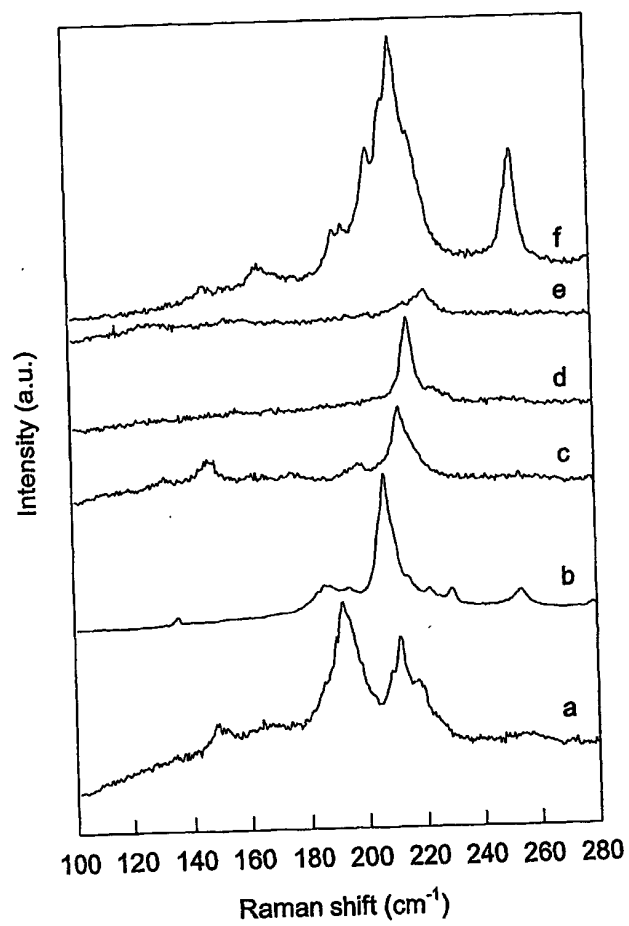


FIG. 4H

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**FIG. 5**

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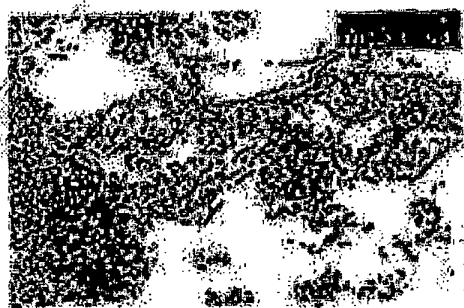


FIG. 6A



FIG. 6B



FIG. 6C

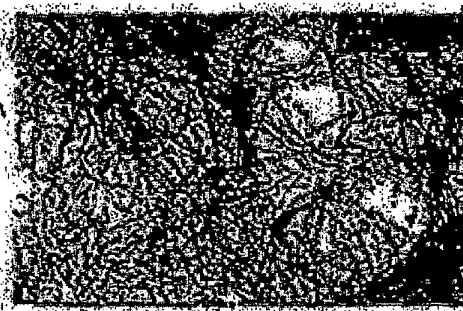


FIG. 6D

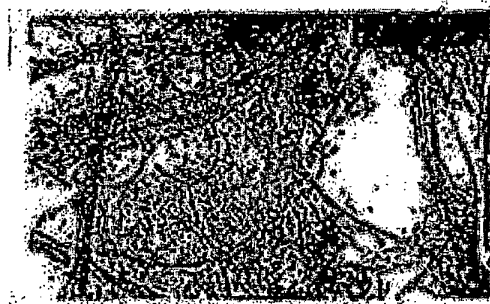
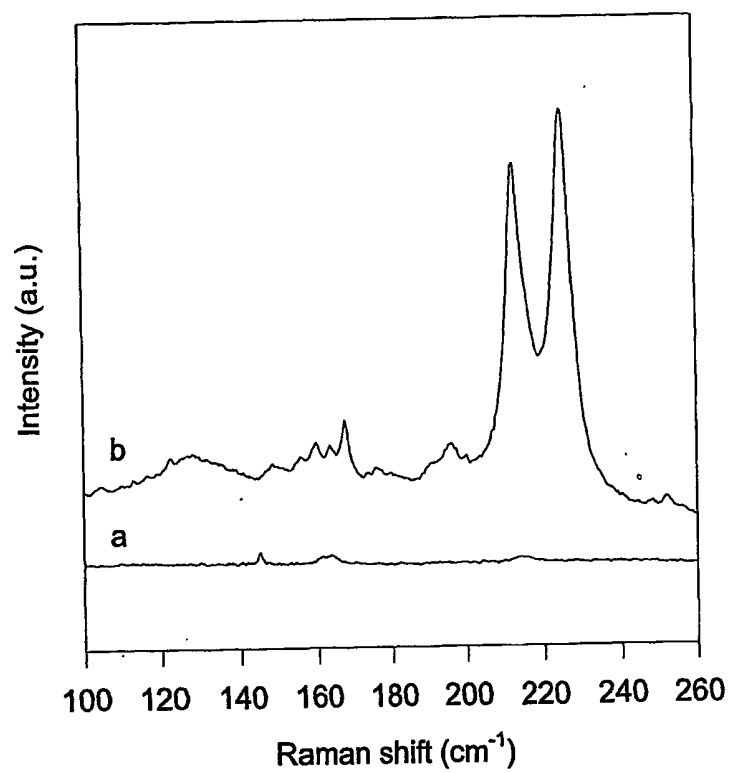


FIG. 6E

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**FIG. 7**

INTERNATIONAL SEARCH REPORT

 Internatic Application No
 PCT/SG 02/00255

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation, to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 73205 A (THE BOARD OF REGEENTS OF THE UNIVERSITY OF OKLAHOMA) 7 December 2000 (2000-12-07) examples 1-9 claims 1-13, 18, 26, 31-35	1-7, 9-12, 15-17, 21
A		13, 14
P, X	WO 01 94260 A (THE BOARD OF REGENTS OF THE UNIVERSITY OF OKLAHOMA) 13 December 2001 (2001-12-13) claims 1-33 page 30, line 17 -page 31, line 2 page 7, line 15 -page 10, line 24 -/-	1-7, 9-12, 15-17, 21, 22, 24, 25

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

21 January 2003

Date of mailing of the international search report

24/02/2003

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HAFNER J H ET AL: "CATALYTIC GROWTH OF SINGLE-WALL CARBON NANOTUBES FROM METAL PARTICLES" CHEMICAL PHYSICS LETTERS, NORTH-HOLLAND, AMSTERDAM, NL, vol. 296, no. 1/2, 30 October 1998 (1998-10-30), pages 195-202, XP000869784 ISSN: 0009-2614 the whole document	1-3,5,9, 10,15, 16,21
Y		6,8
A		4,17
Y	COLOMER J. F. ET AL.: "Large-scale synthesis of single-wall carbon nanotubes by catalytic chemical deposition (CCVD) method" CHEMICAL PHYSICS LETTERS, vol. 317, no. 1-2, 28 January 2000 (2000-01-28), pages 83-89, XP002227992 cited in the application page 84, left-hand column, paragraph 4 -column D, paragraph 1	6-8
X	KITIYANAN B ET AL: "Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co-Mo catalysts" CHEMICAL PHYSICS LETTERS, vol. 317, no. 3-5, 4 February 2000 (2000-02-04), pages 497-503, XP002227993 ISSN: 0009-2614 cited in the application page 498, line R	1-3,5,9, 15,16
Y		6,7
A		4
X	CASSELL A M ET AL: "Large scale CVD synthesis of single-walled carbon nanotubes" JOURNAL OF PHYSICAL CHEMISTRY. B, MATERIALS, SURFACES, INTERFACES AND BIOPHYSICAL, WASHINGTON, DC, US, vol. 103, no. 31, 5 August 1999 (1999-08-05), pages 6484-6492, XP002226019 ISSN: 1089-5647 cited in the application the whole document	1-3,5,9, 21
A		17

	-/--	

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/SG 02/00255

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	POULSEN P R ET AL: "Single-wall carbon nanotube devices prepared by chemical vapor deposition" ELECTRONIC PROPERTIES OF NOVEL MATERIALS - MOLECULAR NANOSTRUCTURES. 14TH INTERNATIONAL WINTERSCHOOL/EUROCONFERENCE, KIRCHBERG, AUSTRIA, 4-11 MARCH 2000, no. 544, pages 504-507, XP008012738 AIP Conference Proceedings, 2000, AIP, USA ISSN: 0094-243X the whole document	1-3,9,21
X	MATSUMOTO S ET AL: "Selective growth of single-walled carbon nanotubes by chemical vapor deposition" PROCEEDINGS OF THE TSUKUBA SYMPOSIUM ON CARBON NANOTUBE IN COM (CNT10);TSUKUBA, JAPAN OCT 3-5 2001, vol. 323, no. 1-4, 3 October 2001 (2001-10-03), pages 275-276, XP002227903 Phys B Condens Matter;Physica B: Condensed Matter October 2002 the whole document	1-3,9,21
A		17
X	MING SU ET AL: "A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity" CHEMICAL PHYSICS LETTERS, NORTH-HOLLAND, AMSTERDAM, NL, vol. 322, no. 5, 26 May 2000 (2000-05-26), pages 321-326, XP002226018 ISSN: 0009-2614 the whole document	1-3,5,9, 15-17,21
P,X	TANG S ET AL: "Controlled growth of single-walled carbon nanotubes by catalytic decomposition of CH/sub 4/ over Mo/Co/MgO catalysts" CHEMICAL PHYSICS LETTERS, vol. 350, no. 1-2, 14 December 2001 (2001-12-14), pages 19-26, XP002227904 ISSN: 0009-2614 the whole document	1-7, 9-14, 17-21, 24,25
P,X	ZHENG B ET AL: "CVD synthesis and purification of single-walled carbon nanotubes on aerogel-supported catalyst" APPL PHYS A;APPLIED PHYSICS A: MATERIALS SCIENCE AND PROCESSING MARCH 2002, vol. 74, no. 3, March 2002 (2002-03), pages 345-348, XP002227905 the whole document	1-3,5,9, 21,24,25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/SG 02/00255

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0073205	A	07-12-2000	US 6333016 B1	25-12-2001
			AU 5462200 A	18-12-2000
			BR 0011106 A	05-03-2002
			CN 1360558 T	24-07-2002
			EP 1192104 A1	03-04-2002
			WO 0073205 A1	07-12-2000
			US 2002165091 A1	07-11-2002
WO 0194260	A	13-12-2001	US 6413487 B1	02-07-2002
			AU 6529801 A	17-12-2001
			WO 0194260 A1	13-12-2001
			US 2002131910 A1	19-09-2002